

## Poly[[di- $\mu_3$ -acetato-di- $\mu_2$ -aqua-diaqua-di- $\mu_3$ -hydroxo-tricopper(II)] naphthalene-1,5-disulfonate]

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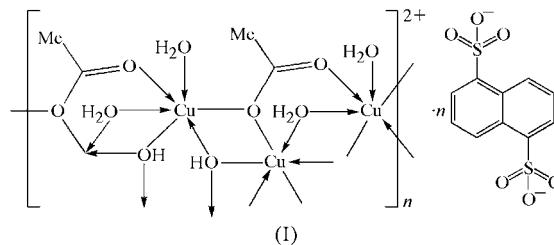
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The crystal structure of the title complex,  $\{[\text{Cu}_3(\text{C}_2\text{H}_3\text{O}_2)_2(\text{OH})_2(\text{H}_2\text{O})_4](\text{C}_{10}\text{H}_6\text{O}_6\text{S}_2)_n\}$ , is built of infinite polymeric cationic  $[\text{Cu}_3(\text{C}_2\text{H}_3\text{O}_2)_2(\text{H}_2\text{O})_4(\text{OH})_2]^{2+}_n$  chains stretching along the  $a$  axis, with naphthalene-1,5-disulfonate (1,5-nds) anions in between. One independent  $\text{Cu}^{\text{II}}$  cation and the 1,5-nds anion occupy special positions on crystallographic inversion centres. Each  $\text{Cu}^{\text{II}}$  cation has an octahedral coordination environment formed by two carboxyl O atoms, two hydroxo O atoms and two water molecules. The carboxylate and hydroxo groups perform a bridging function, linking adjacent Cu atoms in the chain, with a shortest  $\text{Cu}\cdots\text{Cu}$  distance of 2.990 (3) Å. The chains are further linked into a three-dimensional supramolecular framework *via* hydrogen-bonding interactions involving the sulfonate groups of the 1,5-nds dianions.

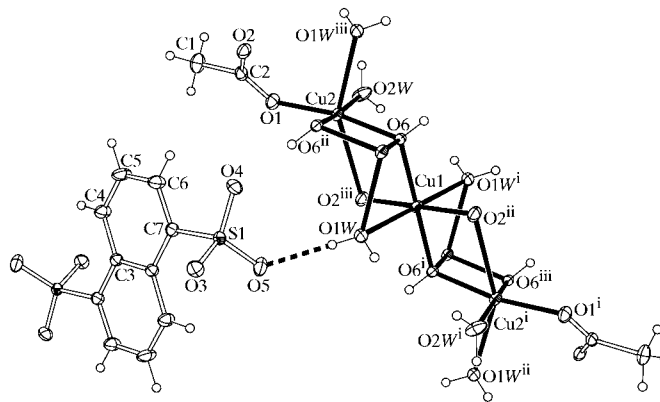
### Comment

The study of the supramolecular chemistry of organosulfonates has received growing attention over the past few years (Côté & Shimizu, 2003). Organosulfonate ions have proved able to generate not only highly robust and fascinating architectures but also 'softer' networks with sponge-like properties by connecting main group and some transition metal ions, such as barium(II) (Cai, Chen, Liao, Feng & Chen, 2001) or silver(I) (Gao *et al.*, 2005). The sulfonate groups are generally incorporated into inorganic–organic networks and are engaged in hydrogen-bond interactions. Naphthalene-1,5-disulfonic acid, with its rigid structure and two functionally active  $\text{SO}_3$  groups in two well separated positions, is known as a good candidate for the construction of supramolecular complexes, particularly as the sulfonate unit has a high propensity to form strong hydrogen bonds (Cai, 2004). To date, many complexes have been reported in which the sulfonate dianions serve as hydrogen-bond acceptors, but most of the cations in these complexes are mono- or dinuclear (An *et al.*, 2004; Cai, Chen, Liao, Yao *et al.*, 2001; Chen *et al.*,

2002). Recently, we have obtained the novel title hybrid complex,  $[\text{Cu}_3(\text{C}_2\text{H}_3\text{O}_2)_2(\text{OH})_2(\text{H}_2\text{O})_4](1,5\text{-nds})$  (1,5-nds is naphthalene-1,5-disulfonate), (I), by the reaction of naphthalene-1,5-disulfonate and copper diacetate monohydrate in an aqueous solution. In (I), an inorganic chain acts as the cation.



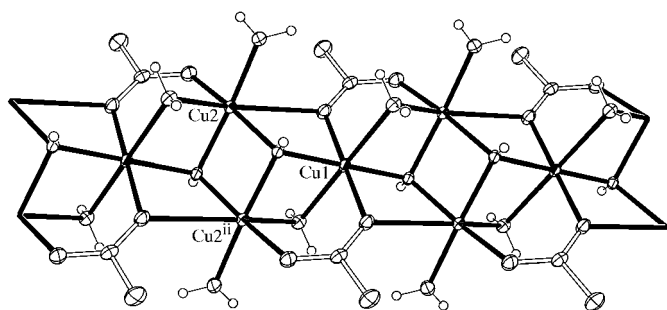
As illustrated in Fig. 1, the crystal structure of (I) contains one  $[\text{Cu}_3(\text{C}_2\text{H}_3\text{O}_2)_2(\text{OH})_2(\text{H}_2\text{O})_4]^{2+}$  cation and one 1,5-nds anion. The two parts are held together *via* hydrogen bonds between water molecules and the O atoms of the 1,5-nds ligand, with an  $\text{O}\cdots\text{O}$  distance and an  $\text{O}-\text{H}\cdots\text{O}$  angle of 2.000 (11) Å and 167 (2)°, respectively. In the cation, each  $\text{Cu}^{\text{II}}$  atom is six-coordinated. Atom Cu1 occupies a special position on a crystallographic inversion centre and has a classic Jahn–Teller-distorted octahedral coordination environment formed by two carboxyl O atoms, two hydroxo O atoms and two water molecules, the latter lying *ca* 0.35 Å further away from the Cu atom. Atom Cu2 has a somewhat less regular octahedral coordination environment, with two carboxyl O atoms, one hydroxo O atom and one water molecule in the equatorial plane [the deviation from the mean plane is 0.2410 (3) Å and the displacement of the Cu atom from this plane is 0.1051 (3) Å]; two of these O atoms are bridging [O6 and O2<sup>iii</sup>; symmetry code: (iii)  $x - 1, y, z$ ]. Another water molecule and a hydroxo O atom lie in the Jahn–Teller elongated axial positions, with an  $\text{O}-\text{Cu}-\text{O}$  angle of 170.43 (6)°. Similar bond distances and angles are observed in these complexes, except that the  $\text{Cu1}-\text{O1W}$  distance is somewhat shorter than the  $\text{Cu2}-\text{O1W}^{\text{ii}}$  distance [symmetry code: (ii)  $-x + 1, -y + 1, -z$ ;



**Figure 1**  
An ORTEP plot (Johnson, 1976) of the title complex, with displacement ellipsoids drawn at the 30% probability level. The dashed line denotes a hydrogen bond. [Symmetry codes: (i)  $-x, -y + 1, -z$ ; (ii)  $-x + 1, -y + 1, -z$ ; (iii)  $x - 1, y, z$ .]

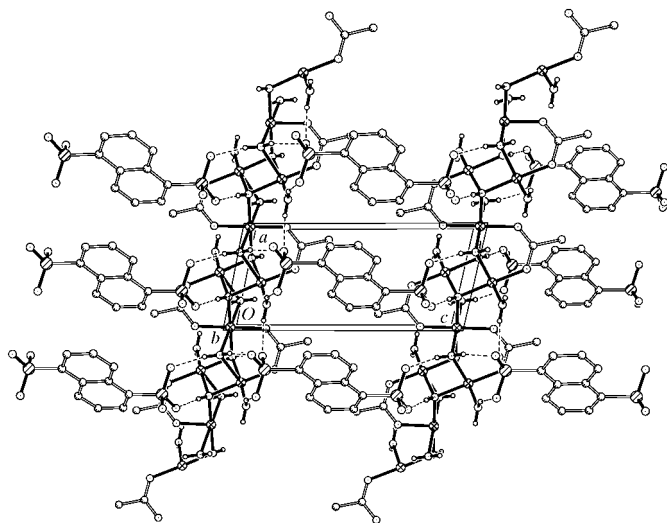
Table 1]. Both the carboxylate groups and the hydroxo groups perform a tridentate bridging function, linking together adjacent Cu atoms into a one-dimensional inorganic chain, with Cu1...Cu2, Cu1...Cu2<sup>ii</sup> and Cu2...Cu2<sup>ii</sup> separations of 3.325 (3), 3.019 (3) and 2.990 (3) Å, respectively (Fig. 2).

The 1,5-nds anion, which lies on an inversion centre, is not engaged in coordination owing to the weak donor ability of the sulfonate group towards transition metal ions. The dihedral angle between the plane of the naphthalene ring system and the plane defined by the three O atoms of the SO<sub>3</sub> group is 115.1 (5)°. The inorganic chain interacts with 1,5-nds anions via O—H...O hydrogen bonds between water molecules, hydroxo O atoms and sulfonate O atoms (Table 2). The structure can be envisaged as one in which layers of anions alternate with layers of cations, the layers being linked via extensive intermolecular hydrogen bonds, giving rise to a three-dimensional network, with alternating 'organic' and 'inorganic' sheets (Fig. 3).



**Figure 2**

The inorganic chain structure of the title complex. H atoms of carboxylate groups have been omitted for clarity. [Symmetry code: (ii)  $-x + 1, -y + 1, -z$ .]



**Figure 3**

The packing of the title complex, viewed along the *b* axis, with the O—H...O hydrogen bonds denoted by dashed lines. H atoms not involved in hydrogen bonding have been omitted.

## Experimental

Copper diacetate monohydrate (0.1 g, 0.5 mmol) was added to an aqueous solution of naphthalene-1,5-disulfonic acid (0.14 g, 0.5 mmol) that had previously been treated with 0.1 M sodium hydroxide to attain a pH of 5. The solution was allowed to evaporate slowly at room temperature, and blue prismatic crystals of (I) were removed from solution by filtration after several days. Analysis calculated for C<sub>14</sub>H<sub>22</sub>Cu<sub>3</sub>O<sub>16</sub>S<sub>2</sub>: C 23.98, H 3.16%; found: C 24.00, H 3.17%.

### Crystal data

[Cu<sub>3</sub>(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>(OH)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]  
(C<sub>10</sub>H<sub>6</sub>O<sub>6</sub>S<sub>2</sub>)  
*M<sub>r</sub>* = 701.06  
Triclinic, *P* $\bar{1}$   
*a* = 5.6035 (11) Å  
*b* = 8.9812 (18) Å  
*c* = 12.119 (2) Å  
 $\alpha$  = 86.31 (3)°  
 $\beta$  = 77.38 (3)°

$\gamma$  = 77.56 (3)°  
*V* = 581.1 (2) Å<sup>3</sup>  
*Z* = 1  
*D<sub>x</sub>* = 2.003 Mg m<sup>-3</sup>  
Mo *K*α radiation  
 $\mu$  = 2.98 mm<sup>-1</sup>  
*T* = 295 (2) K  
Prism, blue  
0.35 × 0.24 × 0.18 mm

### Data collection

Rigaku R-Axis RAPID  
diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan  
(*ABSCOR*; Higashi, 1995)  
*T<sub>min</sub>* = 0.425, *T<sub>max</sub>* = 0.584

5778 measured reflections  
2638 independent reflections  
2481 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.012  
 $\theta_{\text{max}}$  = 27.5°

### Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.019  
*wR* (*F*<sup>2</sup>) = 0.053  
*S* = 1.08  
2638 reflections  
176 parameters  
H atoms treated by a mixture of  
independent and constrained  
refinement

$w = 1/[\sigma^2(F_o^2) + (0.0277P)^2 + 0.3053P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
( $\Delta/\sigma$ )<sub>max</sub> = 0.001  
 $\Delta\rho_{\text{max}}$  = 0.42 e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = -0.32 e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Cu1—O1 <sup>W</sup>	2.3369 (14)	Cu2—O2 <sup>iii</sup>	2.7180 (12)
Cu1—O2 <sup>ii</sup>	1.9629 (12)	Cu2—O2 <sup>W</sup>	1.9664 (15)
Cu1—O6	1.9753 (12)	Cu2—O6	1.9551 (12)
Cu2—O1 <sup>W</sup> <sup>ii</sup>	2.4034 (15)	Cu2—O6 <sup>ii</sup>	1.9663 (14)
Cu2—O1	1.9288 (13)		
Cu2—O6—Cu1	115.56 (6)	O2 <sup>ii</sup> —Cu1—O6	93.85 (6)
O1—Cu2—O1 <sup>W</sup> <sup>ii</sup>	97.38 (5)	O6—Cu1—O1 <sup>W</sup>	85.93 (5)
O1—Cu2—O2 <sup>W</sup>	90.21 (7)	O6—Cu1—O1 <sup>W</sup> <sup>i</sup>	94.07 (5)
O1—Cu2—O6	169.28 (5)	O6 <sup>ii</sup> —Cu2—O1 <sup>W</sup> <sup>ii</sup>	84.32 (5)
O1—Cu2—O6 <sup>ii</sup>	93.29 (6)	O6—Cu2—O1 <sup>W</sup> <sup>ii</sup>	90.83 (5)
O2 <sup>W</sup> —Cu2—O1 <sup>W</sup> <sup>ii</sup>	86.40 (6)	O6 <sup>ii</sup> —Cu2—O2 <sup>W</sup>	170.43 (6)
O2 <sup>iii</sup> —Cu1—O1 <sup>W</sup>	89.16 (6)	O6—Cu2—O2 <sup>W</sup>	97.21 (6)
O2 <sup>ii</sup> —Cu1—O1 <sup>W</sup>	90.84 (6)	O6—Cu2—O6 <sup>ii</sup>	80.62 (6)
O2 <sup>iii</sup> —Cu1—O6	86.15 (6)		

Symmetry codes: (i)  $-x, -y + 1, -z$ ; (ii)  $-x + 1, -y + 1, -z$ ; (iii)  $x - 1, y, z$ .

H atoms on C atoms were placed in calculated positions [ $C-H = 0.93$  Å and  $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$  for aromatic H atoms, and  $C-H = 0.96$  Å and  $U_{\text{iso}}(H) = 1.5U_{\text{eq}}(C)$  for methyl H atoms] and were included in the refinement in the riding-model approximation. The H atoms of the water molecules and hydroxo groups were located in difference maps and refined with O—H and H...H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with  $U_{\text{iso}}(H)$  values of 1.5 $U_{\text{eq}}(O)$ .

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1W-H1W1\cdots O3^{iv}$	0.838 (9)	1.977 (11)	2.7695 (19)	157 (2)
$O1W-H1W2\cdots O5$	0.839 (9)	2.000 (11)	2.824 (2)	167 (2)
$O2W-H2W1\cdots O5^v$	0.85 (2)	2.137 (14)	2.947 (2)	159 (2)
$O2W-H2W2\cdots O3^{vi}$	0.842 (10)	1.840 (10)	2.676 (2)	171 (3)
$O6-H9\cdots O4^{ii}$	0.824 (10)	1.883 (10)	2.7055 (19)	175 (2)

Symmetry codes: (iv)  $-x+1, -y, -z$ ; (v)  $x, y+1, z$ ; (vi)  $x-1, y+1, z$ .

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP II* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3048). Services for accessing these data are described at the back of the journal.

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